THE PREPARATION OF FINE CARBIDE POWDERS FROM COAL SOLUTIONS

David. L. Morgan, Vladimir Cukan and Sara N. Prins
Division of Materials Science and Technology, CSIR
P O Box 395, 0001 Pretoria, South Africa.

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INTRODUCTION

Non-oxide ceramics, such as silicon carbide [1], find use in applications requiring extreme hardness, chemical inertness and high-temperature strength. Transition metal carbides, such as tungsten carbides cemented with cobalt or nickel, are used extensively as wear components. Articles are generally fabricated by sintering pressed powder bodies at high temperatures. To maximise strength and hardness of the ceramic bodies, fine powders below 1 micron in size are needed together with small additions of sintering aids. Boron carbide plus carbon are used as sintering aids for silicon carbide. Very uniform dispersion of the sinter aid or binder metal with the carbide powder is necessary. This is achieved by milling the components together, often for many hours. The carbides are generally prepared by reacting the metal or oxide together with carbon. The low reactivity of particulate carbon means that high temperatures have to be used with extensive milling being required to reduce the particles to a suitable size. The end result of these requirements is that sinterable powders are expensive.

Fine oxide ceramic powders with very uniformly dispersed additives are prepared by the sol-gel process where the components are mixed as solutions or sols and the mixture then gelled [2]. The solvent is removed and the ceramic converted at relatively low temperature to fine, easily-sinterable powder. It would be very desirable to be able to extend those ideas to the preparation of fine carbide powders by bringing a carbon source into very intimate contact with an oxide followed by carbothermal reaction to the carbide e.g.:

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

However no low-cost carbon source has been readily available. Carbohydrates have been used in solution with colloidal silica sols but non-uniform drying could be expected [3]. Polycarbosilanes and silanes may be converted to silicon carbide but are very expensive [4]. Most organic polymers pyrolise to carbon, but generally in low yield.

Coal solutions may be used as an effective and inexpensive source of carbon for the sol-gel preparation of silicon carbide. The coal molecules may also be brought into very intimate contact with the oxide by co-precipitating coal from solution together with an oxide gel under conditions of high shear. This approach is more general as maintaining both coal and metal oxide sol in solution together prior to gelling is not a simple matter. Absorbing coal molecules into a high surface area oxide is also effective. The coal is immobilised by gelling prior to solvent recovery.

We have prepared silicon carbide from coal solution by each of these three approaches [5]. The products from the co-gel and co-precipitation routes were both fine powders, with a very small content of fibrous whiskers whilst that prepared by the mixing route was predominantly fibrous in nature.

X-ray diffraction measurements showed that in all cases the silicon carbide was in the β-form, as would be expected from the low conversion temperature.

COAL SOLUTION

The coal solution was prepared by alkali-induced solubilisation of a medium-volatile bituminous coal in dimethylformamide (DMF) [6,7]. Over 90% of the organic part of suitable coals dissolve in DMF on addition of 10% (based on coal) of sodium or potassium hydroxide. The conditions for extraction are mild-atmospheric pressure,

temperature of 90°C but strict exclusion of oxygen. The mineral components are removed by centrifugation and filtration giving a purified solution of "refcoal". The refcoal solutions used for carbide preparation had typically a concentration of 8% coal-derived material.

Refcoal solution gels on addition of 5% water or sufficient acid to neutralise the alkali present, giving a soft gel strong enough for a cylinder 2cm x 6cm high to be self-supporting.

The refcoal after removal of solvent contained less than 0,2% ash and gave 75% yield of carbon on pyrolysis at 1000°C.

EXPERIMENTAL

The coal used was a flotation concentrate, with essentially all particles being smaller than 0,85 mm. The analysis is given in the Table.

PREPARATION OF COAL SOLUTION

Coal (5,0 kg), DMF (50 kg) and sodium hydroxide pearls (0,5 kg) were stirred together under nitrogen at 90°C for 5 hours. The minerals and undissolved coal were removed by settling followed by filtration through polypropylene filter cloth. The clarified solution contained 8,0% dissolved coal material. The viscosity was 2,9 cP at 30°C.

PREPARATION OF SILICON CARBIDE BY SOL-GEL ROUTE

A silica sol was prepared by mixing ethyl silicate (40% SiO_2, 7,5 kg) in DMF (3,5 kg) with 1% HCl solution in water (1,33 kg). The mixture warmed and became homogeneous over 60 minutes.

The silica sol was cooled to below 5°C and rapidly mixed (within 5 seconds) with coal solution (50 kg), also cooled to below 5°C. The mixture thickened and then gelled. The gel was broken up and the solvent removed under reduced pressure at 95°C to give a coarse powder which was pressed into briquettes (≈ 8 g mass) under high pressure. The briquettes were pyrolised at 900°C for 3 hours and then converted to silicon carbide by heating to 1500°C for 7 hours in a stream of argon (15 l/min). After cooling under argon the briquettes were crushed to smaller than 1 mm and excess carbon burned off at 700°C for 5 hours in a muffle furnace. Measurement of free silica showed 99,5% conversion although this may represent some re-oxidation during carbon burnoff. Sodium salts arising from the alkali present in the coal solution were removed with a dilute acid wash and the product was dried.

The silicon carbide was a fine grey powder. Size analysis gave a median particle size of 1,5 micron. SEM examination showed that the particles were made up of agglomerates of sub-micron particles. Whisker-like particles were virtually absent - a few could be found on active searching.

PREPARATION OF SILICON CARBIDE BY CO-PRECIPITATION ROUTE

Sodium silicate solution (300 ml, containing 18,0 g SiO_2 and 5,45 g Na_2O), sulphuric acid (48 ml, containing 8,5 g H_2SO_4) and coal solution (300 ml) were pumped separately but simultaneously over 5 minutes using peristaltic pumps into a reactor (30 ml) fitted with a high-shear mixer. The overflow of gelatinous co-precipitate was collected and recirculated through the high-shear mixer for 30 minutes at 100 ml/min.

The co-precipitate was dried and sodium sulphate removed by washing with water. The precursor powder was briquetted under pressure and converted to silicon carbide by heating to 1450°C for 6 hours under flowing argon. Conversion of silica was complete. Excess carbon was burned off at 700°C for 5 hours.

The silicon carbide was a fine grey powder with a median particle size of 3,5-5 micron. SEM examination showed that the particles were made up of agglomerates of sub-micron particles. Few whiskers were seen but there were

more than were present in the co-gelled product.

PREPARATION OF SILICON CARBIDE BY MIXING ROUTE

The precipitated silica used was Crosfield Neosyl GP, containing 88% SiO_2 and with a typical BET surface area of 200 m^2/g. Precipitated silica (20,5 g, containing 18 g SiO_2) was mixed with coal solution (300 ml). Water (15 ml) was added to gel the coal solution. The solvent was removed to give a precursor which was converted to silicon carbide as above. The conversion of silica was total.

The silicon carbide after excess carbon burnoff formed a felt of fibrous material. SEM examination showed that the great bulk of the product was fibrous with some interspersed amorphous material.

DISCUSSION

The fineness and freedom from fibrous material of the silicon carbide prepared by the three different approaches from coal solution is clearly affected by the degree of inter-dispersion of the refcoal with the silica. The sol-gel route would be expected to give the highest inter-dispersion of carbon and silica as the components had been mixed together in solution prior to gelling. The mixed precursor might be expected to have the poorest inter-dispersion with the co-precipitated precursor in between. The properties of the silicon carbide prepared from co-precipitated precursor were very similar to that prepared from the co-gel material which suggests that the inter-dispersion was also similar. This augurs well for successfully extending the co-precipitation route to the preparation of other carbides, because control of this method is simpler than that of co-gelling coal solutions with oxide sols. Clearly the properties of the silicon carbide prepared by the co-gel route are better than those of co-precipitate material. However the cost of silica from sodium silicate is very much less than that from ethyl silicate so that our further efforts are being concentrated on optimising the co-precipitation route, and on the introduction of homogeneously dispersed sintering aids.

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TABLE: COAL ANALYSIS

Moisture		0,7%
Ash		10,8
Vol. Mat.		22,6
Fixed carbon		65,9
DAF	carbon	90,5
	hydrogen	5,4
	nitrogen	1,9